ON THE INFRA-RED SPECTRA OF SOLUTIONS OF *O*-CHLOROPHENOL AND PHENOL

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ABSTRACT. The infra-red absorption spectra of solutions of *o*-chlorophenol and phenol in carbon tetrachloride and cyclohexane and also of the pure liquids have been recorded with a Perkin-Elmer Model 21 spectrophotometer in the region from 2800 cm^{-1} to 3700 cm^{-1}. The strong absorption maximum at 3533 cm^{-1} and the low inflexion at 3595 cm^{-1} due to 5% solution of *o*-chlorophenol are found to shift to 3540 cm^{-1} and 3605 cm^{-1} respectively when the solvent is changed from carbon tetrachloride to cyclohexane. As the concentration is increased to 30% a new broader and weaker maximum appears on the lower frequency side of the main peak. In the case of pure liquid two new broad peaks appear with greater height, but the maximum at 3500 cm^{-1} persists and an inflexion at 3600 cm^{-1} is also observed.

In the case of 5% solution of phenol in carbon tetrachloride a sharp peak is observed at 3605 cm^{-1} with a broad and higher maximum at 3380 cm^{-1} and the height of the latter diminishes as the concentration is reduced.

These results have been compared with those reported by previous workers. It has been concluded that the maximum at 3540 cm^{-1} given by the solution of *o*-chlorophenol in cyclohexane is due to valence oscillation in the O-H group in the *trans* configuration and that the assignment of this frequency to the *cis* configuration made by previous workers is not correct mainly for the reasons that the frequency is found to depend on the environment, that the O-H frequency of phenol should be higher than that of free O-H group in *o*-chlorophenol molecule, and that the interval between this maximum and the low peak at about 3600 cm^{-1} remains constant when either the liquid is dissolved in different solvents or the temperature of the solution is changed.

INTRODUCTION

It was first suggested by Pauling (1936) that the two peaks at 6910 cm^{-1} and 7050 cm^{-1} observed in the infra-red spectrum of solution of *o*-chlorophenol in carbon tetrachloride (Wulf and Liddel, 1935) are due to the first harmonic of the valence oscillations of the O-H group in the *cis* and *trans* configurations respectively with respect to the chlorine atom. Later, Davies (1938) investigated the infra-red spectrum in the 2.8μ region of the solution of *o*-chlorophenol in CCl_4 at 18°C and 73°C and observed that at 18°C there was a strong peak at 2.825μ (3540 cm^{-1}) and a very weak peak at 2.775μ (3600 cm^{-1}) and that the intensity of the latter peak increased when the solution was heated to 73°C. He pointed out that these results confirmed the hypothesis of Pauling mentioned above. He

further calculated from the intensity-ratio the energy-difference between the two states and found it to be 1420 cal/mole. Recently, Mukherjee (1958) studied the Raman spectra of solutions of *o*-chlorophenol of different concentrations in different solvents and observed that the intensity of the line 3533 cm^{-1} due to OH valence oscillation in the pure liquid increases when the substance is dissolved in carbon tetrachloride and it increases further with the diminution in the concentration of the solutions. Similar results were observed in the case of solutions in cyclohexane, but the line is situated at 3550 cm^{-1} in this case. He has concluded from these results that as this line is attributed to the OH valence oscillation of the O-H group in the *trans* position, the number of such molecules increases with diminution of concentration of the solution in carbon tetrachloride. He further suggested that the line 3550 cm^{-1} observed in the solution in cyclohexane might represent the frequency of free O-H valence oscillations and that in the solution in carbon tetrachloride the frequency is lowered to 3533 cm^{-1} by the influence of the chlorine atoms in carbon tetrachloride molecules

The frequency 3540 cm^{-1} reported by Davies (1938) in the infra-red spectrum is slightly higher than the Raman frequency 3533 cm^{-1} observed by Mukherjee (1958) in the Raman spectrum of the solution in carbon tetrachloride. Also the influence of different solvents on the infra-red spectrum was not investigated by previous workers. It was further noticed that the energy-difference of the two configurations deduced by Davies for the solution in carbon tetrachloride was much smaller than that for the vapour (Zumwalt and Badger, 1940). It was, therefore, thought worthwhile to find out this influence in solutions of different strengths in different solvents and to correlate the results of such investigations with those on the Raman spectra of the solutions of *o*-chlorophenol published by previous workers. With this object in view studies have been made of the infra-red spectra of solutions of different strengths of *o*-chlorophenol in carbon tetrachloride and cyclohexane and similar investigations on the spectra of phenol have also been carried out for comparison. The influence of temperature on the infra-red spectra of the solutions of *o*-chlorophenol has also been studied.

EXPERIMENTAL

The infra-red spectra were recorded with a Perkin-Elmer Model 21 infra-red spectrophotometer provided with a rock salt prism and wave number scale in the counter. The slit was adjusted by putting the resolution dial at about 916. Atmospheric absorption had to be correctly compensated by adjusting the balance in order to get reliable results. The gain in the amplifier required for satisfactory operation was found to be 6.0. For calibration in the region 3000 cm^{-1}—3800 cm^{-1} the C-H band of benzene at 3046 cm^{-1} was recorded with the double beam arrangement and this band was put at 3046 cm^{-1} in the counter. It was found, however, that when operated as a single beam instrument to record

the atmospheric water band at 3740 cm^{-1} the position of the band indicated by the counter was only about 3732 cm^{-1}. So, no attempt was made to make the counter read correctly beyond 3600 cm^{-1}. The instrument was placed in an air-conditioned room, the temperature of which was maintained at about 27°C.

Chemically pure *o*-chlorophenol purchased from B.D.H. was redistilled under reduced pressure. Phenol of the same quality was purified by repeated crystallisation. Carbontetrachloride and cyclohexane used as solvents were also of chemically pure quality and these two liquids were also distilled in vacuum before being used as solvents.

In the case of *o*-chlorophenol the strengths of the solutions used were 30% and 5% for the solution in carbon tetrachloride and 30%, 5% and 3% for the solution in cyclohexane. The spectrum due to pure *o*-chlorophenol was also recorded for comparison. Similar studies were made with solutions of phenol of strengths 5% and 1% in carbon tetrachloride and 4% and 1% in cyclohexane. The thickness of the cell was 0.1 mm in the case of dilute solutions and .025 mm in the case of the pure liquids and their concentrated solutions

In order to find out whether the position of the absorption maximum due to the solution of *o*-chlorophenol in carbon tetrachloride depends on temperature, the curve due to a 5% solution at 70°C was recorded and compared with the curve recorded for the solution at 27°C. This was a repetition of the investigation made by Davies (1938), but special care was taken to resolve the structure and to find out whether any small shift of the maxima took place with the change of temperature of the solution. A cylindrical electrical heater was used to heat up the cell up to 70°C, the temperature being observed with an ordinary mercury thermometer. Similar investigation was carried out in the case of a 3% solution of *o*-chlorophenol in cyclohexane. Compensation cell was used in the reference beam in the case of all the solutions.

RESULTS AND DISCUSSION

The absorption curves due to *o*-chlorophenol and its solutions of certain concentrations in carbon tetrachloride and cyclohexane at 27°C are reproduced in figure 1. A comparison of the curves II and III due respectively to 30% and 5% solutions of *o*-chlorophenol in carbontetrachloride shows that in the latter case there is a sharp peak at about 3533 cm^{-1} having a very weak maximum at 3595 cm^{-1}. The latter peak is resolved only when full compensation of the atmospheric bands is achieved; otherwise only an inflexion is recorded in this place. In the case of the 30% solutions the maximum is broadened towards lower frequencies and extends up to 3300 cm^{-1}, a new broad peak being present at 3450 cm^{-1}. In the case of the pure liquid the maximum is still broader towards lower frequencies and the absorption in the 3300 cm^{-1} region is very much larger than that in the curve due to the 30% solution. So, it appears

that as the concentration increases, the molecules of *o*-chlorophenol in the solution have greater chance of coming together and the new absorption in the region 3300 cm^{-1} —3450 cm^{-1} is probably produced by some sort of association of molecules. In the case of the pure liquid the maximum absorption is at 3500 cm^{-1} and even at 3300 cm^{-1} the absorption is only slightly less than the maximum, but at frequencies lower than 3300 cm^{-1} the absorption falls off sharply. The nature of the broad absorption peak observed in this case suggests that the peak is produced by superposition of three main broad peaks at 3320 cm^{-1}, 3450 cm^{-1} and 3520 cm^{-1} respectively. There is also an inflexion at 3620 cm^{-1}.

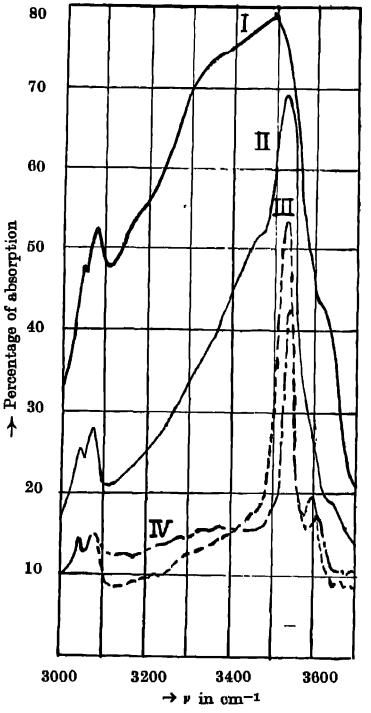

Fig. 1. Infra-red absorption spectra
Curve I. Pure *o*-chlorophenol
„ II. 30% solution of *o*-chlorophenol in CCl_4
„ III. 5% „ „ „ „ „
„ IV. 3% „ „ „ „ cyclohexane.

In the region of first harmonic of this frequency due to pure *o*-chlorophenol in the liquid state Errera and Mollet (1935) observed a peak at 6620 cm^{-1}, there being very small absorption in the region of 7020 cm^{-1}. For a comparison of the results published by them with those observed in the present investigation it is to be found out whether the frequency of the first harmonic is exactly double of the fundamental or it is slightly different. The frequency of the strong fundamental in the solution in carbon tetrachloride is 3533 cm^{-1} at 27°C and not 3540 cm^{-1} as reported by Davies (1938). This discrepancy is due probably to slight error in the calibration of the spectra reported by him. Actual measurement on the peak reproduced by him shows that the frequency may be 3533 cm^{-1}. The frequency of the corresponding harmonic in the dilute solution in carbon tetrachloride reported by Wulf and Liddel (1935) is 6910 cm^{-1}, because the other peak observed by them at 7050 cm^{-1} is only one tenth as intense as the peak at 6910 cm^{-1}. Hence it appears that the frequency of the first harmonic is slightly less than double the fundamental frequency. If such a rule were applied to the frequencies observed in the case of the pure liquid the peak observed by Errera and Mollet (1935) at 6620 cm^{-1} would correspond to a fundamental frequency at about 3385 cm^{-1}, but the maximum observed in the present investigation is at 3500 cm^{-1}. So, there seems to be some discrepancy between the data for the region of the first harmonic and those for the fundamental observed in the present investigation. These latter data show that the funamental O-H frequency is probably altered in the pure liquid due to association of the molecules. Pauling (1945) suggested that the liquid may consist of dimers, and in that case two different O-H frequencies would be expected, one due to the O-H group in which the hydrogen atom is attached to the oxygen atom of the neighbouring molecule and the other due to the O-H group of which the hydrogen is attached to the chlorine atom in the *cis* position in the same molecule. Probably, these two frequencies are respectively 3320 cm^{-1} and 3450 cm^{-1}. Some of the molecules may be associated in a different way in the liquid and the absorption in the 3500 cm^{-1} region may be due to the OH group in these molecules.

The discrepancy between the results reported by Errera and Mollet (1935) and those observed in the present investigation mentioned above can, however, be explained by assuming that a combination frequency due to the C-H and O-H valence oscillations superposed on each other produces a peak at about 6600 cm^{-1} in the absorption curve due to the first harmonic of the broad peak represented by curve I in figure 1. Mukherjee (1958) also suggested that a combination frequency might produce the maximum at 6620 cm^{-1} in the case of the pure liquid.

It can be seen from curve IV in figure 1 that the absorption peak due to 3% solution of *o*-chlorophenol in cyclohexane is at 3540 cm^{-1} and there is a weak broad maximum at 3605 cm^{-1}. A 5% solution also gives similar results and a

30% solution gives new broad maxima as in the case of the 30% solution in carbon tetrachloride. It is thus evident that the position of this weak peak changes from 3595 cm^{-1} to 3605 cm^{-1} when the main peak shifts from 3533 cm^{-1} to 3540 cm^{-1} with the change of the solvent from carbon tetrachloride to cyclohexane. The interval between the main peak and the weak one is thus maintained constant and is about 62 cm^{-1}. The shift of the main peak with the change of the solvent shows that probably the OH group giving this frequency is free and is in the *trans* position, otherwise it would not be affected so much by the molecules of the solvent.

There is another stronger reason to justify this assumption. The frequencies of the second harmonic of the O-H oscillation diminishes by about 100 cm^{-1} when the chlorine atom of the *o*-chlorophenol molecule is replaced by a bromine atom. So, it is expected that when a chlorine atom substitutes a hydrogen atom in the O-H group of the phenol molecule, the O-H frequency should be lowered by more than 30 cm^{-1} in the fundamental mode. As the O-H frequency of the phenol molecule is 3605 cm^{-1}, we can expect a frequency of about 3550 cm^{-1} in the case of free O-H oscillation in *o*-chlorophenol molecule. Actually, we observe a frequency 3540 cm^{-1} in the case of the solution in cyclohexane. The influence of carbon tetrachloride molecules probably lowers the value still further to 3533 cm^{-1} in the solution in carbon tetrachloride. Hence, the assignment of the peak at 3595 cm^{-1} due to the solution in carbon tetrachloride to free O-H oscillation is probably not correct. The curves due to 5% solution of *o*-chlorophenol in carbon tetrachloride at 27°C and 70°C are reproduced in figure 2. It can be seen that at 27°C the main peak is at about 3533 cm^{-1} and the low peak is at about 3595 cm^{-1}, but they shift to 3540 cm^{-1} and 3603 cm^{-1} respectively when the solution is heated to 70°C. These results confirm the view that the influence of carbon tetrachloride molecules lowers the O-H frequency in the solution. At the higher temperature this influence diminishes owing to larger distances between the molecules. The results further show that the weak maximum also shifts by the same amount as the strong one with the change of temperature, and the interval of about 62 cm^{-1} is maintained constant. This indicates that probably the weak peak is due to a combination frequency, one of the frequencies being 3533 cm^{-1} and the other about 62 cm^{-1}. The latter may be that of torsional oscillation of the OH group. So, this maximum is in all probability not due only to the valence oscillation of the free O-H group.

Davies (1938) did not observe any resolved peak at 3595 cm^{-1} in the spectrum due to the solution of carbon tetrachloride at 18°C, but he observed such a maximum when the solution was heated to 73°C. In the present investigation, however, even at 27°C a resolved low peak is observed at 3595 cm^{-1}. As can be seen from figure 2, the height of the maximum does not increase appreciably at 70°C. Hence the value of the ratio of the number of molecules of the *cis* form to that of

trans form calculated by Davies has very little significance. It might be mentioned here that the low maximum is resolved from the main maximum only when

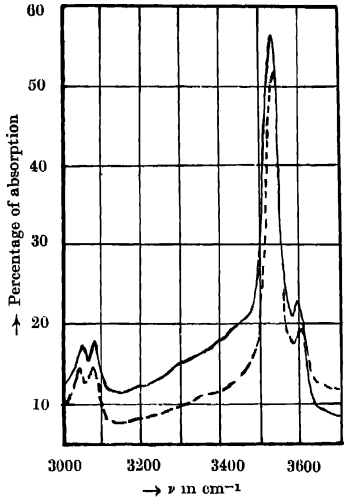

Fig. 2. Infra-red absorption curves.
—— 5% solution of *o*-chlorophenol in CCl_4 at 27°C.
.... „ „ „ „ at 70°C.
(The dotted curve is displaced downwards for clarity).

there is perfect compensation of the bands in the region 3740 cm^{-1} due to water vapour. If there be slight unbalance, the peak disappears and an inflexion is observed in its place. It has also been verified that the solvent used does not give even any weak peak in the whole region between 3000 cm^{-1} and 3800 cm^{-1}. In the case of the solution in cyclohexane no change in the spectrum is observed with the change of temperature.

It is thus observed that the relative intensities of the maxima at 3533 cm^{-1} and 3595 cm^{-1} and the interval between them remain almost constant when the liquid is dissolved in different solvents and the temperature of the solutions is changed. Also in the absorption curve due to the pure liquid the inflexion at 3610 cm^{-1} is distinctly visible. All these results lead to the conclusion that the low peak in the 3600 cm^{-1} region is not due to valence oscillation in the free O-H group but it is due to a combination frequency. The main peak at 3533 cm^{-1} due to the solution in carbon tetrachloride is thus to be assigned to valence oscillation in the free O-H group in the *trans* position. The curve due to the pure liquid shows that this frequency is reduced to about 3500 cm^{-1} and this may

indicate that although the O-H group is in the *trans* position in some of the molecules it is not free but probably it is linked to the chlorine atom of a neighbouring molecule. The frequency is further reduced when the dimer is formed through the O-H linkage as suggested by Pauling (1945).

Comparison with phenol

The curves I and II in figure 3 show that the solution of phenol in carbon tetrachloride gives one broad maximum with its centre at 3380 cm^{-1} and another sharp maximum at 3605 cm^{-1}, besides the sharp peak at 3046 cm^{-1} due to C-H oscillation. The ratio of the heights of the first two peaks diminishes as the concentration is diminished from 5% to 1%. Each of curves III and IV in figure 3 due respectively to 4% and 1% solutions of phenol in cyclohexane, on the other hand, shows a broad maximum at about 3340 cm^{-1} and sharp peak at 3600 cm^{-1}, but the latter peak is lower than that due to solution in carbon tetrachloride. It appears from these results that in phenol the frequency of free O-H valence oscillation is probably 3605 cm^{-1}, but the number of such molecules is small even in

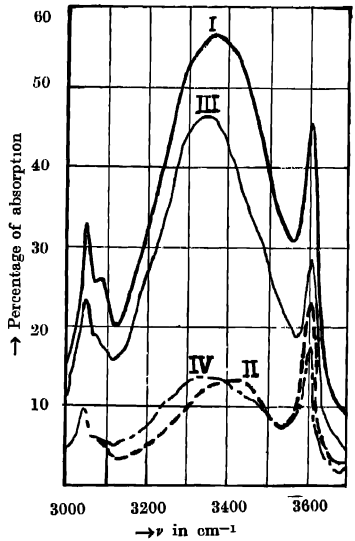

Fig. 3. Infra-red absorption curves of phenol.
Curve I and II. 5% and 1% solutions in CCl_4
Curve III and IV. 4% and 1% solutions in cyclohexane.

4% solution in carbon tetrachloride and in the solution in cyclohexane the number is still smaller. The broad peak at 3340 cm^{-1} may be due to dimers formed by strong association of the molecules. It appears that by the influence of chlorine

atoms in the carbon tetrachloride the dimers are split up into single molecules, but they persist in the solution in cyclohexane. The formation of such dimers or larger associated groups may be responsible for the high viscosity of pure phenol. If the formation of dimers in *o*-chlorophenol in the liquid state through a linkage between the hydrogen atom of the O-H group and the oxygen atom of a neighbouring molecule reduces the O-H oscillation frequency to 3320 cm^{-1} the formation of similar linkage is to be postulated in the case of phenol also, because in this case also the mean O-H frequency of the broad peak is 3320 cm^{-1}. It is interesting that there is no indication of absorption in the region 3450 cm^{-1} in the spectrum due to solution of phenol in carbon tetrachloride while a 30% solution of *o*-chlorophenol in carbon tetrachloride shows a peak at 3450 cm^{-1}. This maximum is therefore to be attributed to the frequency of oscillation in O-H group in the *cis* position with respect to the chlorine atom in the *o*-chlorophenol molecule and no such configuration of the phenol molecule is possible. These results clearly show that the fundamental O-H oscillation in single molecule of phenol has the frequency 3606 cm^{-1}. As pointed out above, the corresponding frequency in the *o*-chlorophenol molecule should be a little less than 3606 cm^{-1} and therefore the frequency 3540 cm^{-1} observed in the spectrum of solution of *o*-chlorophenol in cyclohexane is to be assigned to the free O-H group in the *trans* position.

Comparison of the infra-red and the Raman spectra

It has already been pointed out that the Raman spectrum of *o*-chlorophenol in the liquid state shows only a broad band at 3533 cm^{-1}. The width of the band estimated from the spectra reproduced by Mukherjee (1958) is about 25 cm^{-1}. On the other hand, the corresponding maximum in the infra-red spectrum reproduced in figure 1 has a width more than 300 cm^{-1} and extends from about 3250 cm^{-1} up to about 3600 cm^{-1}. So, the infra-red absorption in the region from 3250 cm^{-1} up to 3500 cm^{-1} is not represented in the Raman spectrum. It could be inferred from these facts that probably the absorption in this region is produced by the O-H oscillation in the dimer proposed by Pauling (1945) and that in the model of the dimer proposed by him the O-H stretching oscillation produces a very small change in the polarisability of the dimer. It can be easily seen from the model that when the stretching oscillations in the two OH groups are in phase the oscillation in the H-O-H group in the dimer is asymmetric. Probably, the oscillation in the two O-H groups in phase is more probable than those in opposite phases. The weak band at 3533 cm^{-1} in the Raman spectrum of the pure liquid is evidently due to the small number of associated molecules of other type and monomers present in the liquid. The increase in the number of single molecules in solutions, as indicated by the maxima in the infra-red spectra reproduced in figure 1, is responsible for the increase in the intensity of the Raman line at 3533 cm^{-1}. The shift of the Raman line due to the solution in cyclo-

hexane observed by Mukherjee (1958) is also confirmed by the curve due to the infra-red spectrum reproduced in figure 1. Thus the results on the investigation on the Raman spectra agree satisfactorily with those on the infra-red spectra.

REFERENCES

Davies, M. M., 1938, *Trans. Faraday Soc.*, **34**, 1427.
Errera, J. and Mollet, P., 1935, *Jour. de Physique*, **6**, 281.
Mukherjee, Deb Kumar, 1958, *Ind. J. Phys.*, **32**, 192.
Pauling, L., 1936, *J. A. C. S.*, **58**, 94.
Pauling, L., 1945, Nature of the Chemical Bond, p. 324.
Wulf, O. R. and Liddel, U., 1935, *J. A. C. S.*, **57**, 1464.
Zumwalt, L. R. and Badger, R. M., 1940, *J. A. C. S.*, **62**, 305.